

(12) **UK Patent Application** (18) **GB** (11) **2 167 192 A**
 (43) Application published 21 May 1988

(21) Application No 8528233

(22) Date of filing 15 Nov 1985

(30) Priority data

(31) 8428934

(32) 15 Nov 1984

(33) GB

(71) Applicant

United Kingdom Atomic Energy Authority (United Kingdom),
 11 Charles II Street, London SW1Y 4QP

(72) Inventors

Dr Patrick Timothy Moseley
 Ronan Alain Stephan
 Dr Jerome Francis McAleer

(74) Agent and/or Address for Service

Clive Stephen Bennett,
 Patents Branch, United Kingdom Atomic Energy
 Authority, 11 Charles II Street, London SW1Y 4QP

(51) INT CL⁴

G01N 25/22 H01L 35/14

(52) Domestic classification

G1N 1A3B 1D4 7A1 7K ACJ
 H1K 2R3F 2S11G 2S17 2S18 2S21 2S22A 2S22C 2S22D
 2S22F 2S26 2S30 2S3A 2S7A 2S7B 2S9 6A2A 6L1 6L3
 6S9 6T1 TA

(56) Documents cited

GB A 2006440 GB 0955019 GB 0249088
 GB 1391514 GB 0924989
 GB 1023561 GB 0815047

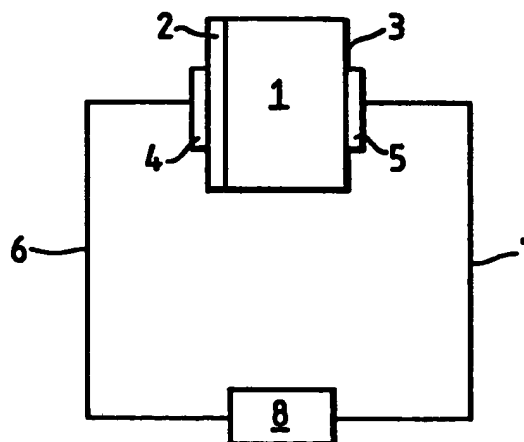
(58) Field of search

G1N
 H1K
 Selected US specifications from IPC sub-class G01N

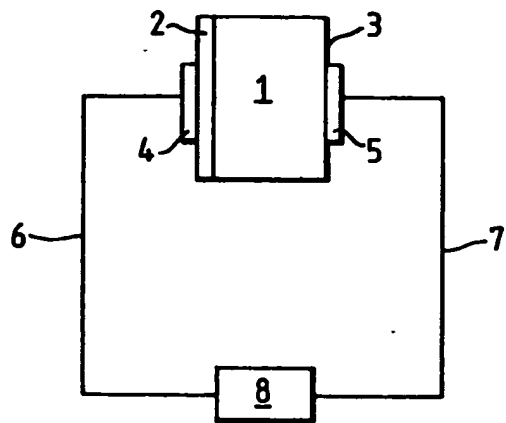
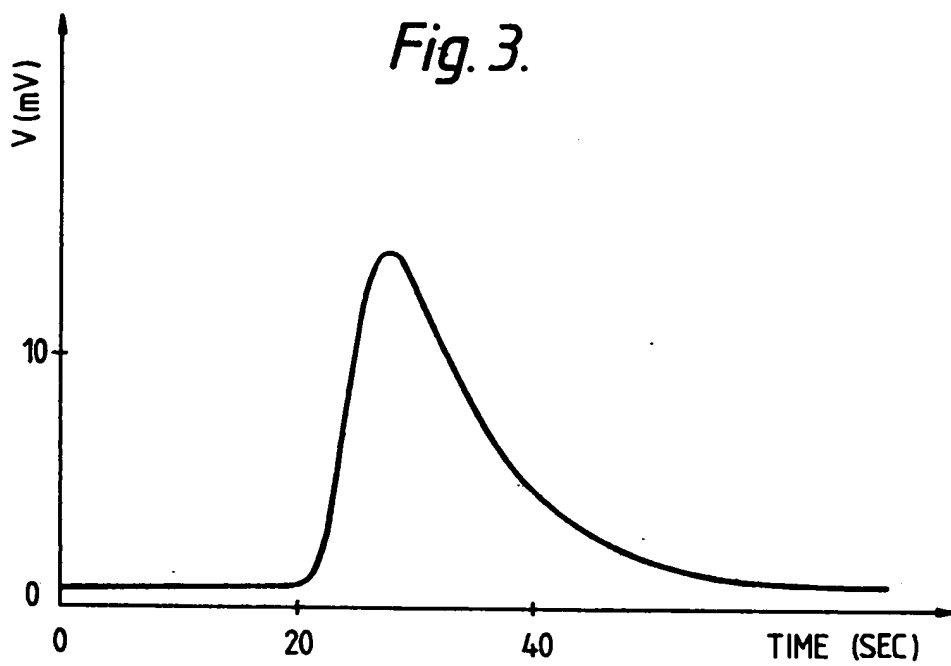
(54) Gas sensor

(57) In a device for sensing gases, such as hydrogen, carbon monoxide, ethylene or hydrogen sulphide, in air, a material 1 has one end coated with a layer 2 for catalysing a desired reaction with the production of heat and thus a temperature differential between the end of the material, and the sensor is arranged to produce a voltage in response thereto by the Seebeck effect. Material 1 may be an oxide semiconductor, e.g. tin dioxide, vanadium pentoxide, chromic oxide, or barium titanate, or are usable with sulphide present, e.g. molybdenum disulphide.

Fig. 1.



GB 2 167 192 A

Fig. 1.*Fig. 3.*

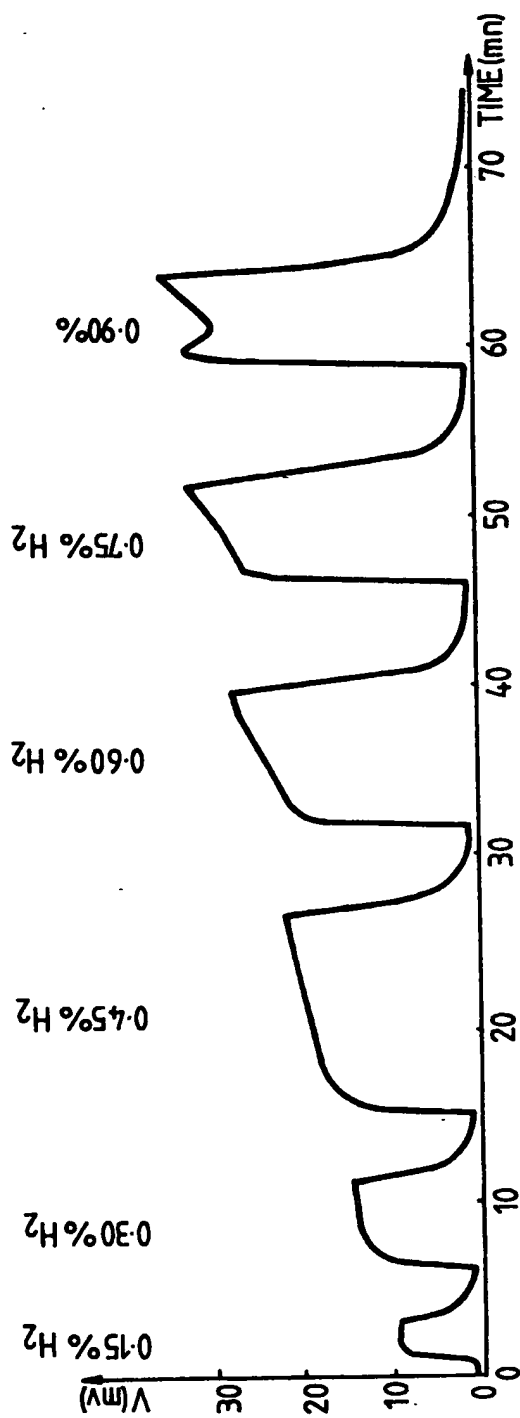
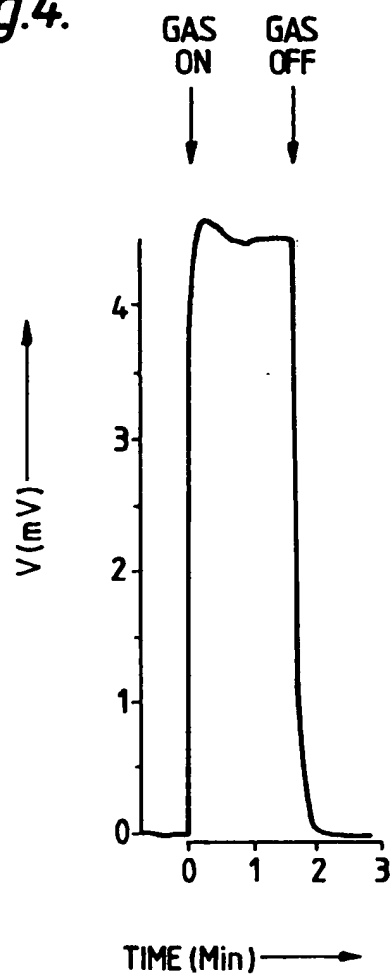


Fig. 2.

Fig.4.



SPECIFICATION

Improvements in or relating to sensors

- 5 The present invention relates to sensors and more particularly to electrical sensor devices which are suitable for use in gases and gaseous mixtures.

- 10 According to one aspect of the present invention there is provided an electrical sensor device which includes a material capable of exhibiting a Seebeck effect, said material being a semiconductor oxide material or a material capable of sensing a sulphide, having a first region and a second region, one of the regions being capable of catalysing a given chemical reaction such that a difference in temperature may be developed between the first region and the second region in order that a Seebeck voltage may be developed between the first and second regions.

The sensor device may include a means for measuring the Seebeck voltage.

- 25 Examples of semiconductor oxide materials which may be used in sensor devices in accordance with the present invention are tin dioxide, vanadium pentoxide, chromic oxide, and barium titanate. Molybdenum disulphide is a further example of material suitable for use in accordance with the present invention as a material capable of exhibiting a Seebeck effect. Molybdenum disulphide may be used in sensing sulphides (e.g. hydrogen sulphide). It is to be understood that some semiconductor oxide materials may be capable of sensing a sulphide.

- 40 In this Specification "capable of sensing a sulphide" is used to embrace materials which are capable of exhibiting a Seebeck voltage when incorporated in a sensor device in accordance with the present invention and contacted with a sulphide in a gas or gaseous mixture.

- 45 A region of the material may be arranged to be capable of catalysing a chemical reaction by provision thereon of a catalytic material.

- 50 Thus, for example, a metallic catalyst such as platinum, platinum-palladium, iridium or ruthenium may be provided at a region of the material.

- By way of example a sensor device of the present invention may be used to detect, in air, gases such as hydrogen, carbon monoxide, C_2H_4 and H_2S .

- 55 It is preferred that the material capable of exhibiting a Seebeck effect is porous in order to provide adequate surface area for contact with a gas or gaseous mixture.

- 60 Also, porosity can facilitate the retention of heat produced during a catalysed reaction.

- 65 An electrical sensor device in accordance with one embodiment of the present invention may comprise a pellet of material capable of exhibiting a Seebeck effect, said material being a semiconductor oxide material or material

- 70 capable of sensing a sulphide, having a region provided with a catalytic material and a region not having a catalytic material, and means for measuring a Seebeck voltage between the two regions.

- 75 Surface parts of the pellet not provided with a catalytic material may, optionally, be provided with a protective coating (e.g. of Au) to protect against possible "poisoning" by reaction products.

- 80 The means for measuring a Seebeck voltage may be, for example, a voltmeter (e.g. a digital voltmeter) the input impedance of which is selected to be sufficiently low that a rest voltage in air is avoided but sufficiently high that no significant current is drawn from the material.

- 85 In one embodiment of the present invention a pellet for use in accordance with the present invention may be prepared by pressing the material capable of exhibiting a Seebeck effect in powder form to give a porous pellet.

- 90 A catalytic material may be sputtered onto a region of the material to provide a region having a catalytic material.

- 95 In another embodiment of the present invention a pellet for use in accordance with the present invention may be prepared by pressing a material, capable of exhibiting a Seebeck effect, in powder form and a mixture of said material in powder form and a catalytic material in powder form such that a porous pellet is formed having a region with a catalytic material and a region not having a catalytic material.

- 100 Thus, for example in accordance with the immediately foregoing embodiment of the invention a material, capable of exhibiting a Seebeck effect, in powdered form may be introduced into a die and a mixture of said material in powdered form and a catalytic material in powder form may then be added to the die to give two regions of powdered material is the die. Pressing may then be carried out to give a porous pellet having a region a catalytic material and a region not having a catalytic material.

- 105 It is to be understood that an electrical sensor device in accordance with the present invention can operate at substantially room temperature and thus the requirement of providing a heating means may be avoided.

- 110 It is to be understood, however, that if desired a sensor device in accordance with the present invention may be operated at an elevated temperature. Thus, for example, a sensor device in accordance with the present invention may be operated at, for example, around $100^\circ C$. An increase in magnitude of response and speed of response may be achieved with certain materials at elevated temperatures of around $100^\circ C$ (e.g. the response to hydrogen sulphide of a sensor device having molybdenum disulphide as the material capable of exhibiting a Seebeck voltage

was increased in magnitude and speed by operating at around 100°C). When compared with the power requirements of known devices operating at 300 to 400°C the power requirements for operating a sensor in accordance with the present invention at around 100°C is relatively small.

It is also to be understood that since the measured voltage is developed by a temperature difference between regions of the material (Seebeck effect) the requirement of providing an external electrical supply as is necessary in the case of a sensor working on, for example, resistivity changes, is substantially avoided (i.e. a device in accordance with the present invention may be substantially "self-powered").

It will be appreciated that in operation a gaseous mixture may be passed over a sensor device in accordance with the present invention and at a region carrying a catalytic material a chemical reaction may occur (e.g. the combustion of gases such as H_2 , CO, C_2H_4 or H_2S) which gives rise to an increase in temperature whilst another region of the material (not carrying a catalytic material) may remain at substantially ambient temperature. The resulting temperature difference gives rise to a voltage by virtue of the Seebeck effect and the voltage is measured. The magnitude of the voltage is related to the concentration in the gaseous mixture of gas which gives rise to the chemical reaction. Thus it is possible, for example, to detect gases (e.g. H_2 , CO, C_2H_4 and H_2S) in air.

Sensor devices in accordance with the present invention are believed to be less prone to moisture "poisoning" than are resistance modulating devices.

The invention will now be further described, by way of example only, with reference to the accompanying drawings and with reference to the Examples 1 to 8.

In the Drawings:

Figure 1 is a diagrammatic representation of an electrical sensor device in accordance with the invention;

Figure 2 shows the voltage response of an electrical sensor device in accordance with the invention to varying concentrations of hydrogen in air;

Figure 3 shows the voltage response of an electrical sensor device in accordance with the present invention to a 5 second pulse of 1% hydrogen in air; and

Figure 4 shows the voltage response of an electrical sensor device in accordance with the present invention to hydrogen sulphide in air.

Referring now to Fig. 1, there is shown an electrical sensor device comprising a cylindrical pellet 1 of material capable of exhibiting a Seebeck effect having, region 2 coated with a catalytic material and a region 3 not coated with a catalytic material. Electrodes 4 and 5 are provided and are connected via conduc-

tors 6 and 7 respectively to a voltage measuring means 8.

In operation a gaseous mixture containing a gas to be detected is passed over pellet 1 and a chemical reaction involving the gas is catalysed at region 2 with a resulting rise in temperature.

A Seebeck voltage is developed between the region 2 and region 3 due to the temperature difference between the regions 2 and 3 and the voltage is measured by voltage measuring means 8.

Examples 1 to 6

A sensor device of the form shown in Fig. 1 of the accompanying drawings was used to detect hydrogen in air.

The sensor device had a pellet of tin dioxide having a region having a Pt-Pd catalyst. Two Au electrodes were sputtered onto opposite end faces of the pellet (i.e. one electrode was formed on a Pt-Pd catalyst and one electrode was formed on a region not having a catalyst). The electrodes were connected to a voltage measuring device (DVM) via Cu wires. The pellet was formed by pressing a layer of tin dioxide powder and a layer of tin dioxide powder mixed with powdered platinum and palladium in a die. The pellet after pressing had a region of porous tin dioxide and a region of porous tin dioxide provided with a platinum-Pd catalytic material.

The pellet was placed in an enclosure and alternately air containing a given hydrogen content and argon was passed over the pellet.

When air containing hydrogen was passed over the pellet a chemical reaction was catalysed by the catalytic material at the region coated with Pt-Pd catalyst giving a rise in temperature. A Seebeck voltage developed between this region and the region not provided with a catalytic material which remained substantially at room temperature.

The response of the sensor is given in Fig. 2 wherein the Seebeck voltage developed is shown for samples of air containing various amounts of hydrogen.

The amounts of hydrogen were 0.15% (Example 1), 0.30% (Example 2), 0.45% (Example 3), 0.60% (Example 4), 0.75% (Example 5) and 0.90% (Example 6).

The samples of air containing hydrogen were alternated with argon.

Example 7

A sensor device of the type used in Examples 1 to 6 was exposed to a 5 second pulse of 1 per cent H_2 in air and the response measured. The response is shown in Fig. 3.

Example 8

A sensor device of the form shown in Fig. 1 of the accompanying drawings was used to detect hydrogen sulphide in air.

The sensor device had a pellet of molyb-

denum disulphide having a region having a Pt-Pd catalyst. Two Au electrodes were sputtered onto opposite end faces of the pellet (i.e. one electrode was formed on a region having a Pt-Pd catalyst and one electrode was formed on a region not having a catalyst). The electrodes were connected to a voltage measuring device (DVM) via Cu wires. The pellet was formed by pressing a layer of molybdenum disulphide powder and a layer of molybdenum disulphide powder mixed with powdered platinum and palladium in a die. The pellet after pressing had a region of porous molybdenum disulphide and a region of porous molybdenum disulphide provided with a platinum-Pd catalytic material.

The pellet was placed in an enclosure and heated to about 110°C and air was passed over the pellet.

When air containing 1000 ppm hydrogen sulphide was passed over the pellet a chemical reaction was catalysed by the catalytic material at the region coated with Pt-Pd catalyst giving a rise in temperature. A Seebeck voltage developed between this region and the region not provided with a catalytic material which remained substantially at room temperature.

The response of the sensor is given in Fig. 4 wherein the Seebeck voltage developed is shown for air containing 1000 ppm hydrogen sulphide at 110°C.

It will be appreciated that "Gas On" and "Gas Off" in the Figure indicate, respectively, the point in time at which air containing 1000 ppm hydrogen sulphide was introduced to the sensor and the point in time at which air containing 1000 ppm hydrogen sulphide was replaced by air.

CLAIMS

1. An electrical sensor device which includes a material capable of exhibiting a Seebeck effect, said material being a semiconductor oxide material or a material capable of sensing a sulphide, having a first region and a second region, one of the regions being capable of catalysing a given chemical reaction such that a difference in temperature may be developed between the first region and the second region in order that a Seebeck voltage may be developed between the first and second regions.

2. An electrical sensor device as claimed in Claim 1 wherein the material capable of exhibiting a Seebeck effect is tin dioxide, vanadium pentoxide, chromic oxide, barium titanate or molybdenum disulphide.

3. An electrical sensor device as claimed in Claim 1 or Claim 2 wherein a metallic catalyst is provided at a region of the material.

4. An electrical sensor device as claimed in Claim 3 wherein the metallic catalyst is platinum, platinum-palladium, iridium or ruthenium.

5. An electrical sensor device as claimed in

any one of Claims 1, 2, 3, or 4 wherein the material is such that the sensor is capable of detecting hydrogen, carbon monoxide, C_2H_4 or H_2S .

6. An electrical sensor device as claimed in any one of the preceding claims wherein the material is porous.

7. An electrical sensor device as claimed in any one of the preceding claims comprising a pellet of material capable of exhibiting a Seebeck effect, said material being a semiconductor oxide material or a material capable of sensing a sulphide, having a region provided with a catalytic material and a region not having a catalytic material, and means for measuring a Seebeck voltage between the two regions.

8. An electrical sensor device as claimed in Claim 7 wherein surface parts of the pellet not provided with a catalytic material are provided with a protective coating.

9. An electrical sensor device as claimed in Claim 7 or Claim 8 wherein the pellet is prepared by pressing the material capable of exhibiting a Seebeck effect in powder form to give a porous pellet.

10. An electrical sensor device as claimed in Claim 7 or Claim 8 wherein the pellet is prepared by pressing a material, capable of exhibiting a Seebeck effect, in powder form and a mixture of said material in powder form and a catalytic material in powder form such that a porous pellet is formed having a region with a catalytic material and a region not having a catalytic material.

11. An electrical sensor device substantially as hereinbefore described with reference to Fig. 1 of the drawings.

12. An electrical sensor device substantially as hereinbefore described with reference to any one of Examples 1, 2, 3, 4, 5, 6, 7, or 8.

Printed in the United Kingdom for
Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings,
London, WC2A 1AY, from which copies may be obtained.